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(74) Agent: **ALLENS ARTHUR ROBINSON PATENT  
AND TRADE MARKS ATTORNEYS**; Stock Exchange  
Centre, 530 Collins Street, Melbourne, VIC 3000 (AU).

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(71) Applicant (*for all designated States except US*):  
**MEGACHEM PTY LTD** [AU/AU]; 49 Nicholas Drive,  
Dandenong South, VIC 3175 (AU).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **PEARSON,  
Graeme, Richard** [AU/AU]; 49 Nicholas Drive, Dandenong South, VIC 3175 (AU). **MORRISON, John, David** [AU/AU]; 49 Nicholas Drive, Dandenong South, VIC 3175 (AU).

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(54) Title: EMULSIFIERS FOR EXPLOSIVE COMPOSITIONS

(57) Abstract: The application relates to a product formed by the reaction of: a) one or more fatty acid esters of alcohols selected from the group consisting of hexitols and their cyclic or bicyclic anhydrides and pentitols and their anhydrides and mixtures thereof; and b) one or more conjoining agents capable of conjoining the fatty acid esters. The conjoining agents may also have two or more reactive functional groups wherein at least one functional group is capable of conjoining with the fatty acid esters and at least one functional group is capable of reacting with a multifoliate initiator. The product may be suitable for using as an emulsifier in a water-in-oil emulsion explosive and other industrial products.



**WO 02/055184 A1**

## Emulsifiers for explosive compositions

### Field of the invention

The invention relates to a novel chemical product. More particularly, the invention relates to a novel chemical product suitable for use in emulsion explosives.

### 5 Background of the invention

In this specification, where a document, act or item of knowledge is referred to or discussed, this reference or discussion is not to be taken as an admission that the document, act or item of knowledge or any combination thereof was at the priority date:

- (a) part of common general knowledge; or
- 10 (b) known to be relevant to an attempt to solve any problem with which this specification is concerned.

Whilst the following discussion relates to explosives, it will be understood that the invention is not limited to explosives and has other applications. In particular the invention may be used in relation to other chemical systems or commodities, particularly water-in-oil emulsions of the  
15 type used in lubricants, adhesives, cutting fluids, foodstuffs, cosmetics and pharmaceuticals. Furthermore, while the following discussion describes the novel product of the present invention when used as an emulsifiers in chemical systems such as water-in-oil or oil-in-water emulsions, the novel product is not so limited, but may act in other capacities in other chemical systems. For example the product may impart advantageous characteristics to  
20 lubricants and adhesives to which it is added.

Detonation is the fast combustion of a substance which is initiated rapidly. When detonated, an explosive undergoes a rapid chemical change and produces a volume of gas which is large compared to the volume of the original explosive. The volume and velocity of the gas produced exerts great pressure on its surroundings.

25 Emulsion explosives (also known as "water-in-oil" emulsion explosives) are referred to as emulsions because they contain liquids that are not miscible in each other, so that one liquid is dispersed as droplets in the other liquid. In an emulsion, the liquid which is in droplet form is referred to as the discontinuous phase, whilst the other liquid is referred to as the continuous phase. If the emulsion is not stabilized, the droplets may separate out and the liquids separate

into discrete layers and the explosive will fail to detonate. An emulsifier (also referred to as a surface active agent or surfactant) is added to stabilise the emulsion and prevent this formation of discrete layers.

Whilst the following discussion relates to bulk explosives, the invention may also be used in  
5 other applications, including packaged explosives.

Bulk explosive emulsion products consist of precursors, which are usually mixed together to form the final products at the mine site. The precursors commonly include an emulsion phase and ammonium nitrate prill.

The emulsion phase comprises:

- 10 (i) a discontinuous aqueous phase comprising discrete droplets of an aqueous solution of inorganic oxygen-releasing salts,
- (ii) a continuous water-immiscible organic phase throughout which the droplets are dispersed, and
- (iii) an emulsifier which forms an emulsion of the droplets throughout the  
15 continuous organic phase.

In the "emulsion phase" of an emulsion explosive, the discontinuous phase is commonly a supersaturated aqueous solution of an oxidizer such as ammonium nitrate (referred to herein as AN) although optionally, other nitrates may be included such as calcium nitrate (referred to herein as CN) and/or sodium nitrate (referred to herein as SN). The continuous phase is an  
20 organic compound which also acts as a fuel. The emulsion phase also contains an emulsifier. The emulsion phase itself is generally not considered to be an explosive. An explosive is formed when the emulsion phase is sensitised, for example, with glass or plastic microballoons, gas bubbles or other void material.

To improve the storage stability of an emulsion, it is necessary to effectively stop coalescence  
25 or crystallisation of the droplets. Emulsifiers are used to inhibit the coalescence of the droplets.

There are two methods to effectively limit crystallisation. The first method involves binding the water in the droplet. This is commonly achieved by adding CN to the discontinuous phase. The second method involves changing the surface monolayer around the droplet and  
30 thus creating an impermeable barrier between the droplets which stops crystals growing from

one droplet into another droplet. Substances which can modify the monolayer include waxes, polymers and emulsifiers.

In some countries, the second method is preferred because of the expense of CN. In addition, the use of CN is believed to have a detrimental affect on the amount of energy released during detonation. In an AN composition, all of the oxygen available for reaction in the explosion is in a gaseous state, therefore this is a high energy composition. CN, on the other hand, forms solids which reducing the energy released.

However, there are countries where CN is not more expensive than AN. Further, since an ideal product with 100% efficiency is rare, some AN/CN formulations may be as efficient as AN only compositions. This is because there are differences between the emulsions formed with AN/CN mixture formulations and AN only formulations.

One of the first emulsifiers used were simple sorbitan mono oleates. However, these emulsifiers did not provide sufficient long term stability. Further research led to the formation of various soaps and oxazolines as emulsifiers, but these emulsifiers were not compatible with the internal and external stabilizers in AN which often cause the emulsions to break and fail to detonate. These emulsifiers were followed by poly(isobutenyl)succinic anhydride derivatives and related compounds (all referred to herein as **PIBSA derivatives**) which are more compatible with the stabilizers in AN production and in single salt explosive emulsion formulas allowing cheaper raw materials. However, PIBSA derivatives are based on petroleum raw materials and used at higher addition rates. As a result they are becoming more expensive and ultimately will be harder to obtain. PIBSA derivatives are used at about 1.5 to 2 wt% in the emulsion whereas (renewable resource vegetable or animal based) sorbitan monooleates are used at 0.8 to 1.0 wt%.

AN prill refers to solid AN granules which have a diameter of 1.5 to 3 mm which is available in grades with different functional qualities. The grades range in density and the type and level of additives, such as anticaking agents. Grades suitable as fertilizer are usually not suitable for explosive purposes. Pure grades are suitable for use in explosives but can be expensive, dangerous to transport and difficult to handle.

However, production of AN is usually tailored to the needs of the customer by choosing appropriate density and additives. For example, crystal modifiers facilitate high AN

production rates and are also used in promoting high density or strong (but porous) low density prill.

One favored crystal habit modifier is naphthalene sulphonate and its derivatives such as Galoryl AT 725 (registered trade mark) which is believed to be the reaction product of sulphurising naphthalene, followed by neutralisation. For example, the naphthalene sulphonate derivative Galoryl AT 725 is often present in the AN at about 300 ppm, (in exceptional cases, over 600 ppm).

However, naphthalene sulphonate and its derivative such as Galoryl AT 725 are often referred to as 'emulsion poisons' because they cause two major problems in emulsion explosives:

- (a) they promote crystal growth in the supersaturated discontinuous phase, which, if allowed to progress, inhibits efficient explosion; and
- (b) they cause coalescence of the discontinuous phase by attacking the bi-layer which results in total failure of the explosive.

The more common failure Galoryl AT 725 is crystallisation of the AN in the aqueous droplets of an AN emulsion. Whether used in AN or AN/CN emulsions, the conventional sorbitan monooleate (SMO) type emulsifiers are rarely compatible with the presence of Galoryl AT 725 at 300 ppm or higher in the AN. PIBSA derivatives usually cope better than SMO with both problems (a) and (b) but these emulsifiers are more expensive and moreover are used at higher rates. However, Galoryl AT 725 has even caused some PIBSA derivative formulations to fail.

There are other additives which may be present in AN, such as clays and aluminium sulphate, and these additives may also reduce the stability of the emulsion.

In addition, waste gear/sump oils are often collected and offered for sale as a cheap fuel oil for emulsion explosive use. These oils often contain variable amounts of additives which may interfere with emulsion stability when sorbitan monooleate type emulsifiers are used.

Since emulsion explosives were developed several decades ago, there have been a myriad of attempts to produce an emulsifier that successfully forms an emulsion, is compatible with all emulsion components yet suppresses crystallisation. For example US 4110134 (Wade) is an early patent describing a water-in-oil emulsifier derivable from sorbitol by esterification with removal of one molecule of water such as sorbitan fatty acid esters. Wade discloses other

useful materials for emulsifier formation including mono- and diglycerides of fat-forming fatty acids, as well as polyoxyethylene sorbitol esters, such as polyethylene sorbitol beeswax derivative materials and polyoxyethylene(4)lauryl ether, polyoxyethylene(2)ether, polyoxyethylene(2)stearyl ether, polyoxyalkylene oleate, polyoxyalkylene laurate, oleyl acid phosphate, substituted oxazolines and phosphate esters, mixtures thereof and the like.

US-3713919 (Tomic) describes emulsifying agents used to form water-in-oil explosive emulsions, such as sorbitan fatty acid esters, e.g., sorbitan monolaurate, palmitate or oleate; polyoxyethylene sorbitol esters and long chain fatty acids and esters thereof.

US-4398976 (Nippon Oil & Fats) relates to emulsifiers capable of forming a water-in-oil emulsion, including fatty acid esters of sorbitan, such as sorbitan monolaurate, sorbitan monooleate, sorbitan monopalmitate, sorbitan monostearate, sorbitan sesquioleate, sorbitan dioleate, sorbitan trioleate and the like; mono- or di-glycerides of fatty acid, such as stearic acid monoglyceride and the like; fatty acid esters of polyoxyethylenesorbitan, such as polyoxyethylenesorbitan monolaurate, polyoxyethylenesorbitan monostearate and the like; oxazoline derivatives; imidazoline derivatives; and the like.

The more recent development of non-ionic 'gemini' surfactants is described in US-6204297. While the aforementioned conventional surfactants generally have one hydrophilic group and one hydrophobic group, 'gemini' surfactants have at least two hydrophobic groups and at least two hydrophilic groups have been introduced. (See also Chemtech, March 1993, pp 30-33), and J. American Chemical Soc., 115, 10083-10090, (1993)). Gemini surfactants are also discussed in US-2374354 (Kaplan); US-2524218 (Bersworth); US-2530147 (Bersworth) (two hydrophobic tails and three hydrophilic heads); US-3244724 (Guttmann); US-5160450 (Okahara, et al.).

Gemini surfactants are relatively quite new and few species have been reported or disclosed in the prior art. US 5534197 (Scheibel) teaches a method for the preparation of a nonionic gemini surfactant wherein the hydrophilic head is a sugar or carbohydrate while the hydrophobic head is a long chain alkyl, the two joined by a short alkyl chain. US 3,888,797 and, 3,855,156 (both Marumo), disclose a number of nonionic gemini surfactant species in which the hydrophobic portion is comprised of a long chain lower alkyl or alkene while the hydrophilic portion is comprised of an ethoxylate group. US 4892806 (Briggs) and EP



0,688,781A1 (Adams) also disclose sugar-based hydrophilic heads joined to the hydrophobic counterpart by a short chain carbon bridge.

### Summary of the Invention

It has surprisingly been found that the conjoining of sorbitan fatty acid esters will produce an  
5 emulsifier suitable for use in emulsion explosives which addresses some of these problems.

In this specification, the term 'conjoining agent' refers to an organic chemical capable of joining together separate molecules of fatty acid esters directly, or indirectly by use of multifoliate initiators.

In this specification, the term 'multifoliate initiator' refers to substances which direct the  
10 growth of a molecule along several branches keeping the joined fatty acid esters well separated from each other (the fatty acid esters are joined to the multifoliate initiators only via conjoining agents).

According to a first aspect of the invention, there is provided a product formed by the reaction of:

- 15 (a) 40 to 95 % by weight of one or more fatty acid esters of alcohols selected from the group consisting of hexitols and their cyclic or bicyclic anhydrides and pentitols and their anhydrides and mixtures thereof; and
- (b) 5 to 60 % by weight of one or more conjoining agents capable of conjoining the fatty acid esters.

20 'Hexitols' and 'pentitols' will be known to those skilled in the art as belonging to a class of compounds commonly referred to as sugar alcohols. A hexitol contains four hydroxymethylene and two hydroxymethyl groups whereas a pentitol contains three hydroxymethylene and two hydroxymethyl groups.

The reaction of the present invention may form a product comprising a single chemical  
25 species or a range of chemical species.

For example, sorbitan sesquioleate reacted exhaustively with a half molar (or two thirds molar) amount of dicarboxylic acid can form a molecule containing two (or three) moieties of sorbitan sesquioleate. Sorbitan monoleate can be similarly reacted.

Emulsions formed using this product are unusually non-Newtonian in nature. For example, they are mobile under shear/pumping but otherwise a cohesive gel. Therefore, the product is suitable for use in explosives because the product is easy to pump through a hose into a deep borehole, but once located in the hole it will not readily leak into cracks and fissures in the borehole. Furthermore, products having these non-Newtonian characteristics may be suitable for addition to lubricants or adhesives or in other applications such as drilling or cutting fluids which require such high viscosity.

The product works very efficiently at levels as low as 0.25 wt% in the presence of AN having comprising Galoryl AT 725 at a concentration of 300 to 600 ppm. Often no other emulsifier is required to maintain the emulsion. Therefore, the product is cost effective and can significantly reduce the cost of the explosive.

In the systems where the AN contains additives such as clays and aluminium sulphate, the product performs well in AN only systems, AN/CN systems as well as in AN/SN systems. Sodium nitrate is used as a fudge point depressant in cold climates, that is, it has the beneficial effect of lowering the temperature at which crystals first start to form in the droplets of the discontinuous emulsion phase.

In the field, AN/CN formulations are pumped into a borehole at about 40°C. A minimum viscosity of about 25,000 cSt is desired and a range of 25,000 to 35,000 normally encountered.

Throughout this specification the viscosities referred to have been measured on emulsions at 40°C using a Brookfield viscometer, #4 spindle at speed 6 for high viscosity emulsions and 12 for low viscosity emulsions.

The product may be prepared from "100% green" raw material, and if used together with a green continuous phase (for example, alkyl esters of fatty acids or vegetable oils), an environmentally friendly explosive composition may be formed.

According to a second aspect of the invention, there is provided a product formed by the reaction of:

- (a) 40 to 70 % by weight of one or more fatty acid esters of alcohols selected from the group consisting of hexitols and their cyclic or bicyclic anhydrides and pentitols and their anhydrides and mixtures thereof;



- (b) 5 to 25 % by weight of one or more conjoining agents having two or more reactive functional groups wherein at least one functional group is capable of conjoining with the fatty acid esters and at least one functional group is capable of reacting with a multifoliate initiator; and
- 5 (c) 20 to 45 % by weight of one or more multifoliate initiators having three or more reactive functional groups capable of conjoining with the conjoining agents.

With respect to structure, typically fatty acid esters are conjoined adjacent the end of each of the branches of the multifoliate initiators.

- 10 The product according to the second aspect of the invention is suitable for use in explosives. Typically the product is also suitable for use in other water-in-oil emulsion systems such as lubricants, adhesives, cutting fluids, pharmaceuticals and cosmetics and other commodities which require viscous materials.

The fatty acid esters of alcohols selected from the group consisting of hexitols and their cyclic or bicyclic anhydrides and pentitols and their cyclic or bicyclic anhydrides and mixtures thereof (hereafter **fatty acid esters**) may be selected from suitable materials known to those skilled in the art. The fatty acid esters may be formed by reacting the fatty acid with the hexitol or pentitol under dehydrating conditions. For example, sorbitan C8-54 fatty acid esters may be used, that is, the hexitol sorbitol is esterified with the fatty acids. Those skilled in the art will know that many such fatty acids esters may also be prepared directly from a natural triglyceride of the fatty acids (eg vegetable oils and animal fats) or from their alkyl esters (eg methyl esters from canola oil); or via the action of a fatty acyl chloride or fatty acid anhydride on hexitols and/or cyclic hexitol anhydrides. Another suitable hexitol is mannitol and an example of a suitable pentitol is xylitol. The fatty acid moieties may be saturated or unsaturated and include dimerised (C36) and trimerised (C54) fatty acids. Examples of suitable sorbitan fatty acid esters are sorbitan mono cocoate, sorbitan mono tall oil fatty acid ester, sorbitan dioleate, sorbitan sesquioleate and sorbitan mono-oleate. Preferably, sorbitan sesquioleate is used.

- As mentioned previously, in this specification, the term "conjoining agents" refers to an organic chemical capable of joining together separate molecules of fatty acid esters directly, or indirectly by use of multifoliate initiators.

The conjoining agent may be selected from organic chemicals capable of joining together separate molecules of fatty acid esters directly, or indirectly by use of multifoliate initiators. The conjoining agents have two or more reactive functional groups capable of either conjoining the fatty acid esters or, if a multifoliate initiator is used, conjoining the fatty acid  
5 esters with the multifoliate initiator. (In effect, the product includes multiple axes comprised of chains of carbon atoms and other chemical moieties including hetero atoms and functional groups.) Examples are dicarboxylic acids and their anhydrides and tricarboxylic acids and their anhydrides. When used directly, generally dicarboxylic acids can join together two separate fatty acid esters and tricarboxylic acids can join together three such separate fatty acid  
10 esters. These fatty acid esters can have more than one hydroxyl moiety upon which the conjoining agent can act so other species will coexist with these nominated species. Thus a conjoining agent molecule may join more than once with a single fatty acid ester molecule and a single fatty acid ester molecule may have more than one conjoining agent attached. Moreover it may be desirable to leave a small amount of the conjoining agent attached singly.

15 Nevertheless a conjoining agent can join together separate fatty acid ester substances. However, if a multifoliate initiator is used, then the use of acid anhydrides as the conjoining agent is preferred since free acids would result in a high proportion of the conjoining agent joining twice to a multifoliate initiator, inhibiting conjoining of fatty acid esters at that position. Suitable acid anhydrides are maleic anhydride, succinic anhydride, phthalic  
20 anhydride, tetrahydrophthalic anhydride, hexhydrophthalic anhydride, trimellitic anhydride, nadic methyl anhydride and polyisobutenenylsuccinic anhydride. ('Nadic' is a common term for a norborneol anhydride type species.) Preferably, maleic anhydride is used. Whilst acid anhydrides are preferred, certain dicarboxylic acids such as adipic acid, oxalic acid, malonic acid and sebacic acid are also suitable for use. If an unmodified epoxide is used as the  
25 multifoliate initiator then lactic anhydride may be used. Diisocyanates are also suitable conjoining agents.

One example of a conjoining agent with more than two reactive functional groups is a trimer acid. Trimer acids are made by joining three C18 fatty acid approximately midway along the molecule by a variation of the Diels Alder condensation. Dimer acids, which are also formed  
30 during this process, may also be used as conjoining agents.

The fatty acid esters contain hydroxyl bearing cyclic polyol residues (eg sorbitan; isosorbide) upon which the conjoining agent acts, which is small in comparison to the fatty chain. Thus

when conjoined, the fatty chains surround these close packed joined cyclic residues. Use of larger conjoining agents such as dimer and trimer fatty acids distance these cyclic residues giving improved functionality. Alternatively, fatty acid esters may be conjoined indirectly via multifoliate initiators, again separating these cyclic residues to good effect.

- 5 As mentioned earlier, in this specification, the term "multifoliate initiators" refers to substances which direct the growth of a molecule along several branches keeping the joined fatty acid esters well separated from each other (the fatty acid esters are joined to the multifoliate initiators only via conjoining agents).

A multifoliate initiator contains two or more arms upon each of which a conjoining agent may  
10 be attached singly, eg via opening of a cyclic dicarboxylic acid anhydride ring, leaving the remaining carboxylic acid function(s) free to attach fatty acid esters. A multifoliate initiator directs growth of the molecule along several branches rather than as an essentially linear polyester or cross-linked lattice. Suitable multifoliate initiators with three or more functional groups are any molecules comprising three or more otherwise separate carbon (typically  
15 methylene) chains joined at or near a common point or in a generally similar manner to the same smaller moiety; each chain of which contains no less than 8 and no more than 40 sequential atoms (typically but not necessarily exclusively carbon and typically but not necessarily exclusively present as methylene with a terminal methyl or substituted methyl); along at least 2.5 of the three chains one or more reactive sites (eg OH, NH, NH<sub>2</sub>, COOH,  
20 halogen, epoxy etc) positioned not less than 5 sequential atoms from the point of commonality these reactive sites encompassing any appropriate substituted terminal methyl group or sequenced hetero atom. For example, the initiator could be trifoliate, tetrafoliate or hexafoliate.

An example of a trifoliate initiator is castor oil (CAS 8001-79-4). Most castor oil molecules  
25 contain three fatty chains each of which bears a reactive hydroxyl group at carbon atom no 12 (that is, 12 carbons removed from the glycerol core along an 18 carbon chain). In ideal conditions at least one functional group on each conjoining agent will join with a 12 hydroxy group of the castor oil, leaving the remaining functional group(s) to conjoin with the fatty acid esters. Hydrogenated castor oil (CAS 8001-78-3) may also be used.

- 30 Epoxidized soya bean oil (CAS 8013-07-8) and epoxidized linseed oil (CAS 8016-11-3) each may be suitable or yield suitable multifoliate initiators after the opening of the epoxide ring (eg

to form glycols or ether-alcohols) – that is, may yield one, two or more hydroxyl groups per chain held at any of carbon atom nos 9 and 10, 12 and 13, 15 and 16, etc. Similarly an epoxidized castor oil could be readily modified to have three hydroxyls per chain.

Tri(alkylol)propane (eg tri-methylolpropane) triesters of mono or polyunsaturated fatty acids  
5 could, via epoxidation or some other modification, form non-triglyceride trifoliate initiators.

Pentaerythritol tetraesters could form tetrafoliate initiator and dipentahexaoleates could form hexafoliate initiators. Polyglycerol polyricinoleate may also be used as a multifoliate initiator.

Residual organic acidity of the emulsifier may be removed by amidisation, especially if excess conjoining agents are used. If any free acids remain then this small ionisable oil soluble entity  
10 could reduce the performance of the compound of the present invention. For example, ammonia, simple amines, simple alkylolamines, aminoalkylalkylolamines, diamines etc (eg diethylene triamine and triethylene tetramine) could be used in the amidisation. Preferably, diethanolamine is used. Preferably, the amidisation involves a hot reaction step. Without wishing to be bound by theory, it is believed that such amidisation may also encourage the  
15 major species to condense further, thus increasing the size of the conjugate.

In a preferred embodiment, the product further comprises additional ring systems further along the multi-axis of the molecule. The additional ring systems might be added at three or more points, wherever there is a remaining hydroxy function on the fatty acid ester residues attached to the multi-axis molecule. If the emulsifier has been amidised (with diethanolamine,  
20 cyclic primary or secondary amines), there will be two additional hydroxy functions for each amide formed which are available to extend the molecule. Examples of reagents which will react to form these additional ring systems are benzoyl chloride, phenylacetyl chloride, phenylpropanoyl chloride etc and their cyclohexyl analogues, and isocyanates (e.g. toluenediisocyanate, methylcyclohexyldiisocyanate). Alternatively if aminoethylethanolamine  
25 (AEEA) is used for the amidisation then a powerful polar imidazoline ring is formed.

Without wishing to be bound by theory, it is thought that the additional ring systems may enable the emulsifier to bridge monolayers in water-in-oil emulsions thus adding rigidity (these bridges need not be a single span). It is the combination of multiple extensions (from the multifoliate initiators), polar ring systems and non polar chains on each extension which may  
30 enable the bridging. Further, this bridging may increase surface energy or transmit surface

energy, respectively encouraging smaller or more uniform droplets of discontinuous aqueous phase.

According to a third aspect of the invention, there is provided an emulsion phase for use in an emulsion explosive comprising:

- 5 (a) a discontinuous aqueous phase comprising discrete droplets of an aqueous solution of one or more inorganic oxygen-releasing salts;
  - (b) a continuous water-immiscible organic phase throughout which the droplets of aqueous solution are dispersed; and
  - 10 (c) one or more emulsifiers which form an emulsion of the droplets of aqueous solution throughout the continuous organic phase,
- wherein at least one emulsifier comprises the reaction product of fatty acid esters and conjoining agents as described herein.

### Examples

- 15 The invention will now be further illustrated and explained in the following non-limiting examples.

#### Components used in the examples

|                                      |                                       |
|--------------------------------------|---------------------------------------|
| Adipic acid                          | Huntsman Australia Pty Ltd            |
| Aluminium sulphate                   | Ex Lab Supply, Australia              |
| Ammonium nitrate                     | Ex Orica Limited, Australia           |
| Ammonium nitrate pure                | Ex Orica Limited, Australia           |
| Ammonium nitrate prill, low density  | ACRON LDAN ex Acron, Novgorad, Russia |
| Ammonium nitrate prill, high density | ACRON HDAN ex Acron, Novgorad, Russia |

|  |  |
|--|--|
| Ammonium nitrate Denso                                 | QNP prill ex Queensland Nitro Products (Dyno), Australia |
| Biodiesel (methyl soyate)                              | Proctor & Gamble, USA                                    |
| Calcium nitrate monohydrate                            | Ex Campbells Fertiliser, Australia                       |
| Castor oil (trifoliolate initiator)                    | Ex Redox, Australia or Jayant Castor Oil, India          |
| Diesel oil   | Ex Mobil petrol station, Australia                       |
| Diethanolamine (amidisation agent)                     | Ex Huntsman, Australia                                   |
| Flake hydrogenated castor oil (trifoliolate initiator) | Ex Jayant Castor Oil, India                              |
| Filter aid   | Diatomaceous earth ex Swimming Pool Supplies, Australia  |
| Galoryl AT 725   | Ex Lobeco Products Inc, USA                              |
| Lipotin 100 UB   | Lecithin ex Bronson & Jacobs Australia, Lucas Meyer, USA |
| Maleic anhydride (conjoining agent)                    | Consolidated Chemicals Co, Australia                     |
| Pegasol R150   | Mobil Limited, Australia                                 |
| Phosphoric acid  | 81% ex Albright & Wilson, Australia                      |
| Prorex 36  | 100 solvent neutral mineral oil ex Mobil Oil, Australia  |
| Sodium nitrate   | Ex Orica Limited, Australia                              |
| Sorbitan mono-oleate                                   | Span 80 ex ICI Americas                                  |



|                       |   |
|-----------------------|---|
| SSOr                  | Sorbitan sesqui-oleate (Megatan TX) ex<br>Megachem, Australia |
| Trimellitic anhydride | Amoco, Australia  |
| Unidyme 60            | Trimer acid ex Union Camp, USA                                |

**Comparative Examples using SMO only as emulsifier.****Comparative Example 1**

An attempt was made to prepare an emulsion phase for use in an emulsion explosive having  
5 the following composition:

|               | Component             | Amount (g) |
|---------------|-----------------------|------------|
| Aqueous phase | Ammonium nitrate pure | 210.5      |
|               | Calcium nitrate       | 139.0      |
|               | Galoryl AT 725        | 0.0266     |
|               | Water                 | 71.5       |
| Fuel phase    | Diesel oil            | 75.0       |
|               | SMO                   | 4.0        |

The aqueous phase was stirred together with heating to 60°C to form an essentially clear solution, then allowed to cool to 40-45°C before use. The fuel phase was mixed with slight warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily  
10 over about 10-15 seconds. High speed stirring was continued until an emulsion formed.

The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C. Crystals started to form in the emulsion almost immediately and the emulsion was quite solid and completely crystallised within 2 hours.

**Comparative Example 2**

An attempt was made to form an emulsion phase for use in an emulsion explosive as follows.

|               | Component        | Amount (g) |
|---------------|------------------|------------|
| Aqueous phase | Ammonium nitrate | 360        |
|               | Galoryl AT725    | 0.216      |
|               | Water            | 90         |
| Fuel phase    | Diesel oil       | 45         |
|               | SMO              | 5          |

5 The aqueous phase was stirred together with heating to 75°C to form an essentially clear solution, and held so before use. The fuel phase was mixed with slight warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. High speed stirring was continued for over 30 minutes, however the two phases remained separate and did not form an emulsion.

**Examples using the product of the present invention as emulsifier.****10 Preparation of SSO<sub>rw</sub> for use in formation of the emulsifiers**

If non-fatty sorbitol residues are left in the SSO they will form insoluble polyester in the reaction, therefore the sorbitan sesqui oleate was washed prior to use. It would be possible to achieve the same result using absorptive earth filtration or any other method known to those skilled in the art.

15 SSO<sub>Or</sub> (2600g) was heated to 100°C with stirring, then phosphoric acid (20g) was added and the mixture stirred for 10 minutes. The mixture was tested for the absence of base (yellow to bromophenol blue), and then hot brine (100g of NaCl in 500 ml of water) was added and the mixture stirred for 30 minutes at 95 to 105°C. The mixture was left to settle for 3 hours at about 100°C. The bottom layer plus a little emulsion was run off until a clean oil was left. The  
20 oil was dried under vacuum at 100°C until the water content was below 0.15 wt%. Then Filter aid (5g) was added and the mixture stirred and deaerated with vacuum, then filtered to produce a dark clean oil (SSO<sub>rw</sub>).

### Example 1

In this example, poly(SSOrw maleate) was prepared.

SSOrw (540g) and maleic anhydride (74g) were combined, and heated with stirring to 180°C with nitrogen sparging for 2 hours. The mixture was tested for the absence of anhydride absorption on an Fourier transform infra-red (FTIR) spectrometer. The heating with stirring was continued under vacuum at 180 to 210°C for a further 2 hours and then the mixture cooled. The resultant product was a dark viscous liquid with Acid Value 38 (poly(SSOrw maleate)).

### Example 2

10 In this example, poly(SSOrw maleate)DEAmide was prepared from poly(SSOrw maleate) from Example 1.

Poly(SSOrw maleate) (320g) from Example 1 and diethanolamine (25g) were combined and heated with stirring under vacuum to 180 to 200°C and held so for 1 hour. The mixture was cooled and the product was a dark liquid with Acid Value 5 which was more viscous than poly(SSOrw maleate).

### Example 3

In this example, tri(SSOrw) castor oil maleate was formed from castor oil supermaleate (contains excess maleic anhydride).

20 Castor oil (200g) and maleic anhydride (100g) were stirred together at 120 to 140°C for 2 hours. FTIR spectroscopy shows disappearance of the large castor OH absorption at about 3500 cm. The product was a mobile crunchy clear yellow mass (castor supermaleate).

Castor supermaleate (260g) and SSOrw (370g) were stirred together at 140°C for 1 hour. The mixture was then heated to 150 to 190°C and stirred under vacuum with a splash head as an air condenser to return the maleic acid for 2 hours. Then the maleic acid and water was stripped off for 1 hour. The mixture was cooled and the product was a dark viscous liquid with Acid Value 36 (tri(SSOrw) castor oil maleate).

### Example 4

In this example, tri(SSOrw) Castor oil maleate DEAmide was prepared from the tri(SSOrw) castor oil maleate from Example 3.

Tri(SSOrw) castor maleate from Example 3(330g) and diethanolamine (20g) were stirred under vacuum at 175 to 195°C for 1 hour. The mixture was cooled and the product was a dark very viscous liquid/paste with Acid Value 4.

### Example 5

- 5 In this example, tri(SSOrw) hydrogenated castor maleate was prepared from hydrogenated castor super maleate (not as much excess maleic anhydride as castor oil supermaleate).

Flake hydrogenated castor oil (620g) and maleic anhydride (279g) were stirred together for 3 hours at 120°C. The product was a yellow very viscous crunchy mobile mass, but not solid, with Acid Value 195 (*hydrogenated castor supermaleate*).

- 10 Hydrogenated castor supermaleate (450g) and SSOrw (550g) were stirred together under vacuum at 160 to 180°C with a splash head for 4 hours. The mixture was then heated at 210°C for 2 hours stripping off maleic acid. The product was a dark very viscous liquid with Acid Value 34 (*tri(SSOrw) hydrogenated castor maleate*).

### Example 6

- 15 In this example, tri(SSOrw) hydrogenated castor maleate DEAmide was prepared from the tri(SSOrw) hydrogenated castor maleate from Example 5.

- Tri(SSOrw) Hydrogenated castor maleate from Example 5 (500g) and diethanolamine (35g) were stirred under vacuum with heating from 120°C to 180°C in about 30 to 45 minutes, then cooled immediately. The product was a dark scoopable tacky just mobile rubber with Acid  
20 Value 7.

### Example 7

In this example, tri(SSOrw) castor oil trimellitate was prepared from castor trimellitate and illustrates a product incorporating additional ring systems along the axes of the product.

- Castor oil (100g) and trimellitic anhydride (60g) were stirred together for 2 hours at 140°C,  
25 becoming a white paste (*castor oil trimellitate*).

Castor oil trimellitate (160g) and SSOrw (373g) were stirred together for 2 hours at 190 to 210°C using bubbled nitrogen to remove reaction water. The reaction was then continued using vacuum and stirring at 220°C for 2 hours. The mixture was then cooled to leave a final product with Acid value 25. (*tri(SSOrw) castor oil trimellitate*).

**Example 8**

In this example tri(SSOrw) castor oil trimellitate diethanolamide was prepared from the tri(SSOrw) castor oil trimellitate from Example 7.

5 Tri(SSOrw) castor oil trimellitate from Example 7 (300g) and diethanolamine (15g) were stirred together under vacuum with heating to 180°C, held at 170 to 190°C for 1 hour and then cooled.

**Example 9**

In this example, the tri(SSOrw) ester of a trimer acid was prepared.

10 UNIDYME 60 (300g) and SSOrw were stirred together under vacuum then heated from 160°C to 260°C over 3 hours. The mixture was then cooled to leave a product with Acid Value 34 (*tri(SSOrw) ester of trimer acid*).

**Example 10**

In this example, tri(SSOrw) ester of trimer acid diethanolamide was prepared from the tri(SSOrw) ester of trimer acid from Example 9 as a 75% concentrate in diesel oil.

15 Tri(SSOrw) ester of trimer acid from Example 9 (300g), diethanolamine (24g) and diesel oil (100g) were stirred together with heating to 160°C for 1 hour. The mixture was then cooled to form a dark transparent ropy gel.

**Example 11**

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component                            | Amount (g) |
|---------------|--------------------------------------|------------|
| Aqueous phase | Ammonium nitrate prill, low density  | 105.25     |
|               | Ammonium nitrate prill, high density | 105.25     |
|               | Calcium nitrate                      | 139.0      |
|               | Water                                | 71.5       |
| Fuel phase    | Diesel oil                           | 75.0       |
|               | Example 2 emulsifier                 | 4.0        |

20 The aqueous phase was stirred together with heating to 60°C to form an essentially clear solution, then allowed to cool to 40-45°C before use. The fuel phase was mixed with slight warming (30-40°C).



Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. High speed stirring was continued until an apparent maximum viscosity was achieved or 3 minutes, whichever was quicker. The final viscosity was about 20,000 cSt at 40°C.

- 5 The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained essentially unchanged.

### Example 12

- 10 An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component             | Amount (g) |
|---------------|-----------------------|------------|
| Aqueous phase | Ammonium nitrate pure | 210.5      |
|               | Calcium nitrate       | 139.0      |
|               | Galoryl AT 725        | 0.0266     |
|               | Water                 | 71.5       |
| Fuel phase    | Diesel oil            | 75.0       |
|               | Example 3 emulsifier  | 4.0        |

The aqueous phase was stirred together with heating to 60°C to form an essentially clear solution, then allowed to cool to 40-45°C before use. The fuel phase was mixed with slight warming (30-40°C).

- 15 Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. High speed stirring was continued until an apparent maximum viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity was about 28,000 cSt at 40°C.

- 20 The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained essentially unchanged.

It is noted that the emulsion of Example 12 has the same composition as the emulsion of Comparative Example 1 except that the emulsifier is a product of the present invention rather than SMO. While the emulsion of Example 12 shows good resistance to crystallisation over a long period of time, the emulsion of the Comparative Example 1 had crystallised completely after only 2 hours. This illustrates the fact that an emulsifier of the prior art such as SMO, is not compatible with a naphthalene formaldehyde based additive such as Galoryl AT 725, whereas the product of the present invention is compatible.

### Example 13

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component                            | Amount (g) |
|---------------|--------------------------------------|------------|
| Aqueous phase | Ammonium nitrate prill, low density  | 105.25     |
|               | Ammonium nitrate prill, high density | 105.25     |
|               | Calcium nitrate                      | 139.0      |
|               | Water                                | 71.5       |
| Fuel phase    | Diesel oil                           | 75.0       |
|               | Example 4 emulsifier                 | 4.0        |

The aqueous phase was stirred together with heating to 60°C to form an essentially clear solution, then allowed to cool to 40-45°C before use. The fuel phase was mixed with slight warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. high speed stirring was continued until an apparent maximum viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity was about 43,000 cSt at 40°C.

The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained essentially unchanged.

**Example 14**

An emulsion phase for use in an emulsion explosive was formed as follows.

|               | Component             | Amount (g) |
|---------------|-----------------------|------------|
| Aqueous phase | Ammonium nitrate pure | 210.5      |
|               | Calcium nitrate       | 139.0      |
|               | Galoryl AT 725        | 0.0644     |
|               | Water                 | 71.5       |
| Fuel phase    | Diesel oil            | 75.0       |
|               | Example 4 emulsifier  | 2.0        |
|               | Prorex 36 100         | 2.0        |

- 5 The aqueous phase was stirred together with heating to 60C to form an essentially clear solution, then allowed to cool to 40-45C before use. The fuel phase was mixed with slight warming (30-40C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10 - 15 seconds. high speed stirring was continued until apparant maximum  
10 viscosity achieved or 3 minutes, whichever the quicker. The final viscosity was about 37,000 cSt at 40°C.

The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained  
15 essentially unchanged.

**Example 15**

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component            | Amount (g) |
|---------------|----------------------|------------|
| Aqueous phase | Ammonium nitrate     | 361.2      |
|               | Aluminium sulphate   | 0.271      |
|               | Water                | 90.3       |
| Fuel phase    | Diesel oil           | 42.7       |
|               | Example 4 emulsifier | 1.77       |
|               | Lipotin 100UB        | 1.77       |
|               | Prorex 36            | 2.36       |

5 The aqueous phase was stirred together with heating to 75°C to form an essentially clear solution, and held so before use. The fuel phase was mixed with slight warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. high speed stirring was continued until an apparent maximum viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity was >100,000 cSt at 40°C.

10 The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained essentially unchanged.

**Example 16**

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component            | Amount (g) |
|---------------|----------------------|------------|
| Aqueous phase | Ammonium nitrate     | 340.7      |
|               | Sodium nitrate       | 20.5       |
|               | Water                | 90.3       |
| Fuel phase    | Diesel oil           | 42.7       |
|               | Example 4 emulsifier | 2.95       |
|               | Lipotin 100UB        | 2.95       |

- 5 The aqueous phase was stirred together with heating to 65°C to form an essentially clear solution, then held so before use. The fuel phase was mixed with slight warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. high speed stirring was continued until an apparent maximum viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity was >100,000 cSt at 40°C.

- 10 The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained essentially unchanged.

**Example 17**

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component            | Amount (g) |
|---------------|----------------------|------------|
| Aqueous phase | Ammonium nitrate     | 210.5      |
|               | Calcium nitrate      | 139.0      |
|               | Galoryl AT 725       | 0.063      |
|               | Water                | 71.5       |
| Fuel phase    | Diesel oil           | 77.75      |
|               | Example 4 emulsifier | 1.25       |

- 5 The aqueous phase was stirred together with heating to 60°C to form an essentially clear solution, then allowed to cool to 40-45°C before use. The fuel phase was mixed with slight warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. High speed stirring was continued until an apparent maximum  
10 viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity was about 24,000 cSt at 40°C.

The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained  
15 essentially unchanged.



**Example 18**

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component            | Amount (g) |
|---------------|----------------------|------------|
| Aqueous phase | Ammonium nitrate     | 210.5      |
|               | Calcium nitrate      | 139.0      |
|               | Galoryl AT 725       | 0.063      |
|               | Water                | 71.5       |
| Fuel phase    | Diesel oil           | 75.0       |
|               | Example 5 emulsifier | 4.0        |

5 The aqueous phase was stirred together with heating to 60°C to form an essentially clear solution, then allowed to cool to 40-45°C before use. The fuel phase was mixed with slight warming (30-40°C).

10 Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. high speed stirring was continued until an apparent maximum viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity > 100,000 cSt at 40°C.

The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained essentially unchanged.

**Example 19**

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component            | Amount (g) |
|---------------|----------------------|------------|
| Aqueous phase | Ammonium nitrate     | 210.5      |
|               | Calcium nitrate      | 139.0      |
|               | Galoryl AT 725       | 0.063      |
|               | Water                | 71.5       |
| Fuel phase    | Diesel oil           | 75.0       |
|               | Example 6 emulsifier | 4.0        |

5 The aqueous phase was stirred together with heating to 60°C to form an essentially clear solution, then allowed to cool to 40-45°C before use. The fuel phase was mixed with slight warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. high speed stirring was continued until apparant maximum viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity was >  
10 100,000 cSt at 40°C.

The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained essentially unchanged.

**Example 20**

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component              | Amount (g) |
|---------------|------------------------|------------|
| Aqueous phase | Ammonium nitrate Denso | 210.5      |
|               | Calcium nitrate        | 139.0      |
|               | Water                  | 71.5       |
| Fuel phase    | Diesel oil             | 75.0       |
|               | Example 7 emulsifier   | 4.0        |

5 The aqueous phase was stirred together with heating to 60°C to form an essentially clear solution, then allowed to cool to 40-45°C before use. The fuel phase was mixed with slight warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. high speed stirring was continued until an apparent maximum viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity was about  
10 32,000 cSt at 40°C.

The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained essentially unchanged.

**Example 21**

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component              | Amount (g) |
|---------------|------------------------|------------|
| Aqueous phase | Ammonium nitrate Denso | 210.5      |
|               | Calcium nitrate        | 139.0      |
|               | Water                  | 71.5       |
| Fuel phase    | Diesel oil             | 75.0       |
|               | Example 8 emulsifier   | 4.0        |

The aqueous phase was stirred together with heating to 60°C to form an essentially clear solution, then allowed to cool to 40-45°C before use. The fuel phase was mixed with slight warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. High speed stirring was continued until an apparent maximum viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity was about 32,000 cSt at 40°C.

The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained essentially unchanged.

**Example 22**

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component                   | Amount(g) |
|---------------|-----------------------------|-----------|
| Aqueous phase | Ammonium nitrate            | 210.5     |
|               | Calcium nitrate             | 139.0     |
|               | Water                       | 71.5      |
| Fuel phase    | Diesel oil                  | 73.6      |
|               | Example 10 (75%) emulsifier | 5.4       |

The aqueous phase was stirred together with heating to 60°C to form an essentially clear  
5 solution, then allowed to cool to 40-45°C before use. The fuel phase was mixed with slight  
warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily  
over about 10-15 seconds. high speed stirring was continued until an apparent maximum  
viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity was about  
10 50,000 cSt at 40°C.

The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40 °C for  
one week. Examination showed no visual evidence of free oil or free aqueous layer nor did  
the emulsion show visual or tactile evidence of crystal growth. The viscosity remained  
essentially unchanged. Visual re-examination of the emulsion phase after a further 8 weeks  
15 storage at 25 °C showed no change.

Accordingly, examples 11 to 22 illustrate that the compound of the present invention can be  
used to prepare a range of emulsion compositions that are suitable for forming emulsion  
explosives of good stability.

**Example 23**

Sorbitan esters of mixed fatty acids are prepared, reacted with adipic acid and castor oil, subsequently reacted with diethanolamine in the presence of naphthenic mineral oil and adjusted with a heavy aromatic oil.

5 Step A: Sorbitan ester prep

|   |        |
|---|--------|
| Heel (sorbitan ester from an earlier batch) | 200 kg |
| Sorbitol 70/07 (70% sorbitol solution)      | 1375   |
| Methyl esters of vegetable oil (biodiesel)  | 1723   |
| Stearic acid (55%C18, 43%C16)               | 400    |
| Acetic acid                                 | 10     |
| Sodium Hydroxide 46% solution               | 20     |
| Phosphoric acid 81%                         | 40     |

The heel, sorbitol, methyl esters and stearic acid are stirred together and heated to about 130°C during which process the mass dries. The acetic acid and sodium hydroxide are added separately to the mass, a low level nitrogen sparge initiated, and stirring and heating of the mass continued over about 4 hours until a temperature of 235-240°C is reached. Then the  
 10 mass is held stirring at this temperature while the reaction progresses. During these proceedings, reaction water and methanol are evolved, the mass gradually becomes one phase and this uniform liquid exhibits a reducing hydroxyl value as the reaction progresses further.

When the desired degree of reaction is achieved, phosphoric acid is added and after 15 minutes cooling is started. The mass is cooled to about 100°C and settled for several hours  
 15 during which time a small bottom layer of non-fatty sorbitol residues forms which holds much of the sodium phosphate salt formed. The layers are separated.

Step B: Reaction with adipic acid and castor oil.

|                                      |         |
|--------------------------------------|---------|
| Sorbitan esters of mixed fatty acids | 2500 kg |
| Adipic acid                          | 1000    |
| Castor oil                           | 1420    |



- The sorbitan esters, adipic acid and castor oil are stirred together and heated to 200°C. A low nitrogen sparge aids removal of reaction water. Initially the reaction mixture has an Acid Value of about 170 mgKOH/g and this reduces as reaction progresses. The reaction is stopped by cooling aiming at an Acid Value of 35-40. At this stage the product may contain a little solid resinous material formed from sorbitol residues that were not removed from the sorbitol esters earlier. If necessary these can be removed at this stage or after dilution with naphthenic mineral oil (eg by filtration, settling, centrifuge etc). Note also that fast cooling can be achieved by addition of the cold naphthenic oil to the hot reaction mass.

Step C: Completion of the reaction, using diethanolamine.

|   |      |
|---|------|
| Sorbitan ester, adipic acid, castor oil ester | 4700 |
| Prorex 36                                     | 2800 |
| Diethanolamine                                | 350  |
| Pegasol R150 (aromatic mineral oil)           | 400  |

- Prorex 36 is added to the hot reaction product of Step B and when the temperature is below 140°C the diethanolamine is added. The stirred mass is then heated to 180-190°C (again using low nitrogen sparge) and held at this temperature for 1 hour after which the Acid Value is found reduced to negligible levels and the mass cooled. Pegasol R150 is mixed in to aid the flow and miscibility properties (in diesel oil) of the resulting viscous liquid.
- This product has been found suitable for use as the principal emulsifier in a 'AN only' system that replaced a AN/CN system. The requirement was for the emulsion to have at least short term stability when Russian fertiliser grade AN prill was augered into it. This prill contains a powerful crystallisation promotor – believed to be a bis-(naphthalene) sulphonate which often caused emulsions in contact with it to fail within hours. Some countries have laws prohibiting in ground storage of bulk prepared explosives so 'load and shoot' conditions apply. This means that the explosive must be detonated virtually as soon as all the boreholes at a blast site are filled and the explosive does not get to 'sleep' or rest long term in the borehole prior to firing. Long term emulsion stability is thus irrelevant. About 1% or less of this emulsifier was used together with about 0.5% or less of a PIBSA derivative emulsifier. Without the PIBSA derivative emulsifier the emulsion was too viscous for proper augering with on site equipment. Full explosive formulation details not available.

The emulsifier is intrinsically less costly than full strength PIBSA derivative emulsifiers and used in lower amounts. In addition, CN is often less cost effective than AN.

### Example 24

Sorbitan esters of mixed fatty acids are prepared, reacted with trimer acids in the presence of a mineral oil, subsequently reacted with diethanolamine and further adjusted with the mineral oil.

#### Step A: Sorbitan ester prep

|  |      |
|--|------|
| Sorbitol 70/07 (70% sorbitol solution)     | 1025 |
| Methyl esters of vegetable oil (biodiesel) | 645  |
| Methyl esters of tallow                    | 525  |
| Oleic acid                                 | 465  |
| Sodium Hydroxide 46% solution              | 10   |
| Sodium Hypophosphite powder                | 4    |
| Phosphoric acid 81%                        | 20   |
| Sodium Chlorite 40%                        | 27   |
| Water                                      | 400  |
| Salt                                       | 100  |

Sorbitol, methyl esters and oleic acid are stirred together and heated to about 130°C during which process the mass dries. Sodium hydroxide and sodium hypophosphite are added to the mass, a low level nitrogen sparge initiated, and stirring and heating of the mass continued over about 4 hours until a temperature of 235-240°C is reached and then the mass is held stirring at this temperature while the reaction progresses. During these proceedings, reaction water and methanol are evolved, the mass gradually becomes one phase and this uniform liquid exhibits a reducing hydroxyl value as the reaction progresses further.

When the desired degree of reaction is achieved phosphoric acid is added and after 15 minutes cooling is started. The mass is cooled to about 90°C, bleached with sodium chlorite, washed with prepared brine and settled for several hours during which time a bottom layer of aqueous

non-fatty sorbitol residues forms which holds much of the salts. This bottom layer is removed and the sorbitan esters dried by stirring at 130°C.

Step B: Reaction with trimer acid etc

|                                      |         |
|--------------------------------------|---------|
| Sorbitan esters of mixed fatty acids | 1950 kg |
| Trimer acid (UNIDYME 60)             | 1300    |
| Shell oil P873                       | 2055    |
| Diethanolamine                       | 220     |

- 5 The sorbitan esters, trimer acids and mineral oil are stirred together and heated to 200°C. A low nitrogen sparge aids removal of reaction water. Initially the reaction mixture has an Acid Value of about 55 mgKOH/g and this reduces as reaction progresses. The reaction is stopped by cooling aiming at an Acid Value of 20-25. When cooled to below 140°C the diethanolamine is added and the stirred mass is then heated to 180-190°C (again using low nitrogen sparge) and held at this temperature for 1 hour after which the Acid Value is found  
10 reduced to negligible levels and the mass cooled. More oil and the isotridecyl phosphate is stirred into this very viscous dark semi-adhesive liquid.

This product has been found suitable for use as the sole emulsifier at 1% in AN only emulsions containing 600ppm and 1000ppm (of the AN content) Galoryl AT725 crystal  
15 modifier, such emulsions remaining stable for 1-6 months. Similar emulsions using the Russian AN containing problem quantities of the bis-(naphthalene) sulphonate are stable for many weeks.

One user who required long term stability has converted from a AN/CN PIBSA derivative emulsifier based system to an 'AN only' using 1% of this emulsifier. This emulsion is too  
20 viscous for current auger equipment so when dry AN prill is augered in, the emulsion is mixed 50:50 with the AN/CN emulsion. No other formulation details are available.

The emulsifier is intrinsically less costly than full strength PIBSA derivative emulsifiers and is used in lesser amounts. CN is often less cost-effective than AN.

**Example 25**

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component             | Amount (g) |
|---------------|-----------------------|------------|
| Aqueous phase | Ammonium nitrate      | 360        |
|               | Galoryl AT725         | 0.216      |
|               | Water                 | 90         |
| Fuel phase    | Diesel oil            | 45         |
|               | Example 24 emulsifier | 5          |

5 The aqueous phase was stirred together with heating to 75°C to form an essentially clear solution, and held so before use. The fuel phase was mixed with slight warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. high speed stirring was continued until an apparent maximum viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity was >100,000 cSt at 40°C.

10 The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained essentially unchanged. Visual re-examination after further storage for 8 weeks at 25°C showed no change.

15 This illustrates the successful use of the emulsifier of example 24 in an emulsion comprising AN only with Galoryl AT725.

It is noted that Example 25 has the same composition as the emulsion of Comparative Example 2, except that the emulsifier is a product of the present invention rather than SMO. While the composition of Example 25 forms a good emulsion which is resistant to  
20 crystallisation over a long period of time, the composition of the Comparative Example 1 failed to form an emulsion. This illustrates the fact that an emulsifier of the prior art such as

SMO, is not compatible with a naphthalene formaldehyde based additive such as Galoryl AT 725, whereas the product of the present invention is compatible.

### Example 26

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component             | Amount (g) |
|---------------|-----------------------|------------|
| Aqueous phase | Ammonium nitrate      | 360        |
|               | Galoryl AT725         | 0.108      |
|               | Water                 | 90         |
| Fuel phase    | Diesel oil            | 45         |
|               | Example 24 emulsifier | 2          |
|               | Prorex 36 mineral oil | 3          |

5

The aqueous phase was stirred together with heating to 80°C to form an essentially clear solution, and held so before use. The fuel phase was mixed with slight warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. high speed stirring was continued until an apparent maximum  
10 viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity was >70,000 cSt at 40°C.

The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained  
15 essentially unchanged. This illustrates the successful use of the emulsifier of example 24 in an emulsion comprising AN only with Galoryl AT 725

**Example 27**

An emulsion phase for use in an emulsion explosive was prepared as follows.

|               | Component             | Amount (g) |
|---------------|-----------------------|------------|
| Aqueous phase | Ammonium nitrate      | 210.5      |
|               | Calcium nitrate       | 139.0      |
|               | Galoryl AT 725        | 0.063      |
|               | Water                 | 71.5       |
| Fuel phase    | Diesel oil            | 75         |
|               | Example 24 emulsifier | 2          |
|               | Prorex 36 mineral oil | 2          |

The aqueous phase was stirred together with heating to 60°C to form an essentially clear solution, then allowed to cool to 40-45°C before use. The fuel phase was mixed with slight warming (30-40°C).

Using a high speed kitchen blender in the fuel phase, the aqueous phase was added steadily over about 10-15 seconds. High speed stirring was continued until an apparent maximum viscosity was achieved or 3 minutes, whichever was the quicker. The final viscosity was about 50,000 cSt at 40°C.

The emulsion phase was stored in a sealed transparent plastic container held at 35 to 40°C for one week. Examination showed no visual evidence of free oil or free aqueous layer nor did the emulsion show visual or tactile evidence of crystal growth. The viscosity remained essentially unchanged. Re-examination after 4 weeks showed no change.

The word 'comprising' and forms of the word 'comprising' as used in this description and in the claims does not limit the invention claimed to exclude any variants or additions.

Modifications and improvements to the invention will be readily apparent to those skilled in the art. Such modifications and improvements are intended to be within the scope of this invention.

**THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:**

1. A product formed by the reaction of:
  - (a) 40 to 95 % by weight of one or more fatty acid esters of alcohols selected from the group consisting of hexitols and their cyclic or bicyclic anhydrides and pentitols and their anhydrides and mixtures thereof; and
  - (b) 5 to 60 % by weight of one or more conjoining agents capable of conjoining the fatty acid esters.
2. A product formed by the reaction of:
  - (a) 40 to 70 % by weight of one or more fatty acid esters of alcohols selected from the group consisting of hexitols and their cyclic or bicyclic anhydrides and pentitols and their anhydrides and mixtures thereof;
  - (b) 5 to 25 % by weight of one or more conjoining agents having two or more reactive functional groups wherein at least one functional group is capable of conjoining with the fatty acid esters and at least one functional group is capable of reacting with a multifoliate initiator; and
  - (c) 20 to 45 % by weight of one or more multifoliate initiators having three or more reactive functional groups capable of conjoining with the conjoining agents.
3. A product according to claim 1 or 2 wherein the fatty acid esters of alcohols are formed by reacting a fatty acid with the hexitol or pentitol under dehydrating conditions
4. A product according to claim 1 or 2 wherein the fatty acids esters of alcohols are formed by reaction of a species chosen from the group consisting of natural triglycerides of fatty acids, their alkyl esters and mixtures thereof.
5. A product according to claim 1 or 2 wherein the fatty acid esters of alcohols are formed by reacting a first reactant chosen from the group comprising fatty acyl chlorides and fatty acid anhydrides with a second reactant chosen from the group comprising hexitols, cyclic hexitol anhydrides and mixtures thereof.



6. A product according to claim 1 or 2 wherein the conjoining agent is chosen from the group comprising dicarboxylic acids and their anhydrides and tricarboxylic acids and their anhydrides.
7. A product according to claim 6 wherein the conjoining agent is an anhydride of a dicarboxylic acid or tricarboxylic acid, chosen from the group comprising maleic anhydride, succinic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, hexhydrophthalic anhydride, trimellitic anhydride nadic methyl anhydride and polyisobutenenylsuccinic anhydride.
8. A product according to claim 1 or 2 wherein the conjoining agent is chosen from the group comprising adipic acid, oxalic acid, malonic acid, sebacic acid, lactic anhydride and diisocyanates.
9. A product according to claim 1 or 2 wherein the conjoining agent is chosen from the group comprising dimer acids, trimer acids and mixtures thereof.
10. A product according to claim 2 wherein the multifoliate initiator has three or more functional groups
11. A product according to claim 10 wherein the multifoliate initiator has three or more otherwise separate carbon chains joined at or near a common point or in a generally similar manner to the same smaller moiety.
12. A product according to claim 11 wherein each of the separate carbon chains contains no less than 8 and no more than 40 sequential atoms.
13. A product according to claim 12 wherein along at least 2.5 of the three chains there is located one or more reactive sites positioned not less than 5 sequential atoms from the point of commonality and wherein the reactive sites encompass any appropriate substituted terminal methyl group or sequenced hetero atom.
14. A product according to any one of claims 11 to 13 wherein the carbon chains include one or more ring systems.
15. A product according to claim 2 wherein the multifoliate initiator is selected from the group comprising castor oil, epoxidized castor oil, hydrogenated castor oil, epoxidized soya bean oil and epoxidized linseed oil and mixtures thereof.

16. A product according to claim 2 wherein the multifolate initiator is a glycol or ether-alcohol derived by opening the epoxide ring of a reactant chosen from the group comprising epoxidized castor oil, epoxidized soya bean oil and epoxidized linseed oil.
17. A product according to claim 2 wherein the multifolate initiator is derived from  
5 tri(alkylol)propane triesters of mono or polyunsaturated fatty acids, pentaerythritol tetraesters, dipentahexaoleates and polyglycerol polyricinoleate.
18. A product according to claim 1 or 2 wherein the reaction includes an amidisation step suitable for removing free acids.
19. A product according to claim 18 wherein the amidisation step uses an amidising agent  
10 chosen from the group comprising ammonia, simple amines, simple alkylolamines, aminoalkylalkylolamines, diamines, cyclic primary amines, cyclic secondary amines, aminoethylethanolamine and mixtures thereof.
20. A product according to claim 18 wherein the reaction further includes the step of adding further aromatic systems.
- 15 21. A product according to claim 20 wherein the further step includes the use of reagents chosen from the group comprising benzoyl chloride, phenylacetyl chloride, phenylpropanoyl chloride and their cyclohexyl analogues, and isocyanates.
22. The use of a product according to any of the preceding claims as an emulsifier in a water-in-oil emulsion.
- 20 23. An emulsion phase for use in an emulsion explosive comprising:
- (i) a discontinuous aqueous phase comprising discrete droplets of an aqueous solution of one or more inorganic oxygen-releasing salts;
  - (ii) a continuous water-immiscible organic phase throughout which the droplets of aqueous solution are dispersed; and
  - 25 (iii) one or more emulsifiers which form an emulsion of the droplets of aqueous solution throughout the continuous organic phase,
- wherein at least one emulsifier comprises, a product formed by the reaction of:

- (a) 40 to 95 % by weight of one or more fatty acid esters of alcohols selected from the group consisting of hexitols and their cyclic or bicyclic anhydrides and pentitols and their anhydrides and mixtures thereof; and
- (b) 5 to 60 % by weight of one or more conjoining agents capable of conjoining the fatty acid esters.

24. An emulsion phase for use in an emulsion explosive comprising:

- (i) a discontinuous aqueous phase comprising discrete droplets of an aqueous solution of one or more inorganic oxygen-releasing salts;
- (ii) a continuous water-immiscible organic phase throughout which the droplets of aqueous solution are dispersed; and
- (iii) one or more emulsifiers which form an emulsion of the droplets of aqueous solution throughout the continuous organic phase,

wherein at least one emulsifier comprises, a product formed by the reaction of:

- (a) 40 to 70 % by weight of one or more fatty acid esters of alcohols selected from the group consisting of hexitols and their cyclic or bicyclic anhydrides and pentitols and their anhydrides and mixtures thereof;
- (b) 5 to 25 % by weight of one or more conjoining agents having two or more reactive functional groups wherein at least one functional group is capable of conjoining with the fatty acid esters and at least one functional group is capable of reacting with a multifoliate initiator; and
- (c) 20 to 45 % by weight of one or more multifoliate initiators having three or more reactive functional groups capable of conjoining with the conjoining agents.

25. An emulsion phase for use in an emulsion explosive comprising:

- (i) a discontinuous aqueous phase comprising discrete droplets of an aqueous solution of one or more inorganic oxygen-releasing salts;
- (ii) a continuous water-immiscible organic phase throughout which the droplets of aqueous solution are dispersed; and

(iii) one or more emulsifiers which form an emulsion of the droplets of aqueous solution throughout the continuous organic phase,

wherein at least one emulsifier comprises, a product according to any one of claims 3 to 21.

- 5 26. An emulsion phase according to claim 23 or 24 wherein the emulsifier is chosen from the group comprising, poly(SSOrw maleate)DEAmide, tri(SSOrw) castor oil maleate, tri(SSOrw) castor oil maleate DEAmide, tri(SSOrw)hydrogenated castor maleate, tri(SSOrw) hydrogenated castor maleate DEAmide, tri(SSOrw) castor oil trimellitate, tri(SSOrw) castor oil trimellitate diethanolamide, a tri(SSOrw) ester of trimer acid  
10 diethanolamide.
- 27 An emulsion phase according to claim 24 wherein the emulsifier is chosen from the group comprising the products of reaction of sorbitan esters of mixed fatty acids with trimer acids and diethanolamine.
- 15 28. An emulsion phase according to any one of claims 22 to 27 which includes an additive chosen from the group comprising naphthalene formaldehyde and derivatives thereof.
29. An emulsion phase according to claim 28 wherein the emulsifier comprises 0.25 to 5 wt% of the emulsion.
- 20 30. An emulsion phase according to any one of claims 22 to 27 wherein the at least one inorganic oxygen-releasing salt is chosen from the group comprising ammonium nitrate, calcium nitrate and sodium nitrate.
26. A method of preparing the product of claim 1 comprising the step of reacting one or more fatty acid esters of alcohols with one or more conjoining agents.
27. A method of preparing the product of claim 2 comprising the steps of:
- 25 (a) reacting one or more fatty acid esters of alcohols with one or more conjoining agents, and subsequently
- (b) reacting the reaction product of step (a) with one or more multifolate initiators.
28. A method according to claim 26 which further comprises an amidisation step.

29. A method according to claim 27 which further comprises an amidisation step.
30. A method of preparing the product of claim 28 comprising the step of reacting sorbitan esters of mixed fatty acids with trimer acids in the presence of a mineral oil to form a mixture, and subsequently reacting the mixture with diethanolamine adjusted with the mineral oil.
- 5 31. A method of preparing the product of claim 29 comprising the steps of reacting sorbitan esters of mixed fatty acids with adipic acid and castor oil to form a mixture, and subsequently reacting the mixture with diethanolamine in the presence of naphthenic mineral oil adjusted with heavy aromatic oil.
- 10 32. A method of preparing an emulsion suitable for use in an explosive comprising the steps of:
- (i) forming an aqueous phase by dissolving one or more inorganic oxygen-releasing salts in water;
  - (ii) forming a fuel phase by adding a product of claim 1 or 2 to a water-immiscible organic phase,
  - 15 (iii) adding the aqueous phase to the fuel phase with stirring until droplets of the aqueous solution are dispersed throughout the continuous organic phase, forming an emulsion.
- 20 33. A method of preparing an emulsion suitable for use in an explosive comprising the steps of:
- (i) forming an aqueous phase by dissolving one or more inorganic oxygen-releasing salts in water;
  - (ii) forming a fuel phase by adding a product formed by the method of claim 27 or 28 to a water-immiscible organic phase,
  - 25 (iii) adding the aqueous phase to the fuel phase with stirring until droplets of the aqueous solution are dispersed throughout the continuous organic phase, forming an emulsion.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU02/00030

**A. CLASSIFICATION OF SUBJECT MATTER**Int. Cl. <sup>7</sup>: B01F 17/34, 17/36; C06B 47/14, 23/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN file CA, WPIDS, keywords: hexitol, pentitol, fatty, ester, sorbitol, conjoin?, link?, join?, anhydride, adipic, oxalic, malonic, trimellitic, sebacic, lactic, diisocyanate and similar terms

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                             | Relevant to claim No. |
|-----------|--|-----------------------|
| X         | US 6,063,954, A (DIENER <i>et al</i> ) 16 May 2000<br>column 2 lines 21-25 and 48-49                           | 1,3,5,8               |
| P, A      | WO 01/52976, A2 (THE LUBRIZOL CORPORATION) 26 July 2001<br>Page 2 line 21 - page 3 line 12 and 17, lines 18-21 |                       |
| A         | EP 0 688 781, B1 (EASTMAN KODAK COMPANY) 27 December 1995<br>see whole document                                |                       |

☒ Further documents are listed in the continuation of Box C
 ☒ See patent family annex

|   |  |
|---|--|
| * Special categories of cited documents:  |  |
| "A" document defining the general state of the art which is not considered to be of particular relevance  | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  |
| "E" earlier application or patent but published on or after the international filing date   | "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone   |
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| "O" document referring to an oral disclosure, use, exhibition or other means  | "&" document member of the same patent family  |
| "P" document published prior to the international filing date but later than the priority date claimed  |  |

Date of the actual completion of the international search

8 March 2002

Date of mailing of the international search report

25 MAR 2002

Name and mailing address of the ISA/AU

 AUSTRALIAN PATENT OFFICE  
 PO BOX 200, WODEN ACT 2606, AUSTRALIA  
 E-mail address: pct@ipaaustralia.gov.au  
 Facsimile No. (02) 6285 3929

Authorized officer

DAVID GRIFFITHS

Telephone No : (02) 6283 2628

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU02/00030

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |  |                       |
|---|--|-----------------------|
| Category*   | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A   | US 4,892,806, A (BRIGGS <i>et al.</i> ) 9 January, 1990<br>see whole document      |                       |

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/AU02/00030**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent Document Cited in<br>Search Report |           | Patent Family Member |           |    |         |
|---|-----------|----------------------|-----------|----|---------|
| US  | 6063954   | AU                   | 74940/96  | BR | 9611176 |
|   |           | EP                   | 876200    | WO | 9716242 |
| DE  | 19540320  |                      |           |    |         |
| WO  | 200152976 | AU                   | 200134497 |    |         |
| US  | 4892806   | EP                   | 314425    | JP | 2000142 |
| EP  | 688781    | JP                   | 8041094   | US | 5529897 |
| END OF ANNEX                              |           |                      |           |    |         |